Evaluation of Drinking Water Treatment Technologies for Removal of Endocrine Disrupting Chemicals (EDCs)

• K. Schenck, T. Speth , N. Dugan, and D. Williams, U.S. EPA, ORD, NRMRL • L. Rosenblum, Shaw Environmental and Infrastructure, Inc. • • T. Wiese, Xavier University of Louisiana •

Introduction

A number of the chemicals identified as potential EDCs may be present in surface or ground waters used as drinking water sources due to their introduction from domestic and industrial sewage treatment systems and wet-weather runoff. Many of these compounds have already been shown to be present in surface waters in the U.S., leading to a growing concern over the possible presence of EDCs in drinking waters. Although there has not yet been a determination of risks posed by EDCs in finished waters, it is prudent to explore if strategies already employed to manage other drinking water risks can also manage risks associated with EDCs. This project investigates the efficacy of various drinking water treatment processes in removing EDCs from source waters.

The goal of this project is to provide the information necessary for the selection of drinking water treatment techniques that provide for optimal EDC removal and subsequently reduce human exposure to EDCs. In order to be able to evaluate the ability of conventional and advanced drinking water treatment processes to remove EDCs, appropriate analytical methods for the selected EDCs in several water matrices must be available or developed. Additionally, the applicability of bioassay(s) to evaluate the removal/presence of compounds with endocrine activity in water samples pre- and post-treatment will be evaluated.

Methods/Approach

This research project has four components, three of which are currently in progress. The first is the development of appropriate analytical methods to identify and quantify the EDCs being evaluated in the project. Initially, a set of steroid hormones is being used (Figure 1). All of these hormones, except for dihydrotestosterone, were detected in an occurrence study conducted by the US Geological Survey, in which water samples were collected from 139 streams in 30 states.

The development of the analytical method for the steroid hormones has been completed. The method includes solid phase extraction followed by liquid chromatography/mass spectroscopy (LC/MS). All six of the hormones can be separated on a C18 column, using a single step gradient. Single ion monitoring is used to achieve detection limits in the low ng/L range in organic-free water (Figure 2).

A group of alkylphenolic compounds will be evaluated in the future. The analytical procedure for the alkylphenols is currently being developed. This method includes a solid phase extraction step followed by identification/quantification by LC/MS.

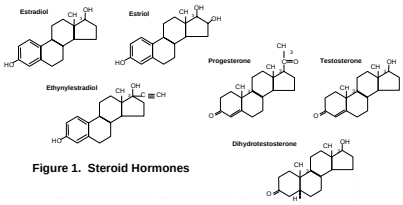

Figure 1. Steroid Hormones

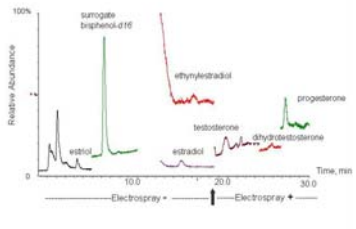

Figure 2. Single Ion Chromatograms of Reagent Water Fortified at 1 ng/L

The second component is the application of a reporter gene assay, the MVLN assay, to evaluate the presence of estrogenic activity in water samples. This assay complements the analytical work, in that it should detect the presence of compounds with estrogenic activity, including those that may be missed analytically due to structural changes in the target compounds during treatment. The MVLN assay uses a human breast cell line which has been stably transfected with the firefly luciferase gene. The presence of estrogenic activity in water sample concentrates is determined by comparing the luciferase activity (light production) of cells following treatment with samples to the activity of cells treated with the steroid hormones. The dose-response curves are shown in Figure 3.

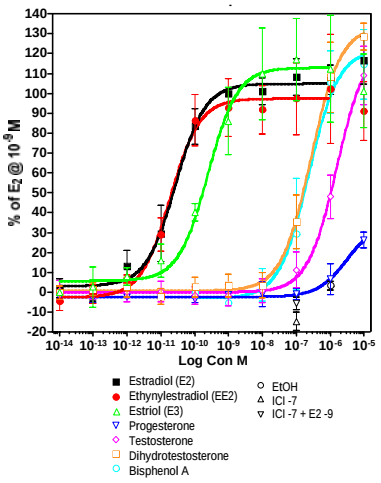

Figure 3. Dose-Response Curves for the Steroid Hormones in the MVLN Assay

The third part of the study is to conduct bench-scale experiments to evaluate the removal of EDCs by various unit processes used in conventional and advanced drinking water treatment. These will include the use of powdered activated carbon (PAC), granular activated carbon (GAC), coagulation, softening, etc. (Figure 4). For each of these processes, pilot-scale evaluations may be conducted in the fourth part of the study, if warranted.

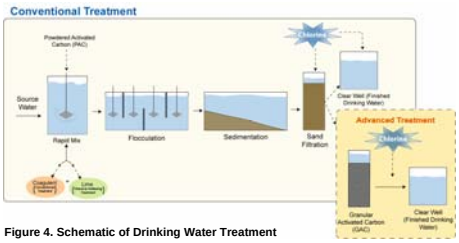

Figure 4. Schematic of Drinking Water Treatment

Results/Conclusions

Activated carbon is used extensively in drinking water treatment for the removal of a broad spectrum of organic contaminants. Consequently, the use of GAC was chosen as the first treatment process to be evaluated at bench-scale for the removal of EDCs from water. In order to predict or model the performance of GAC, several types of information are needed, including the capacity of the carbon for the contaminant of interest. This information is usually obtained from isotherm studies.

GAC isotherm studies have been conducted to determine the capacity of three types of carbon, Norit 1240, Hydrodarco 4000 and SuperDarco 12X40, for ethynylestradiol (EE2). Figure 5 shows bottle-point isotherms for the three carbons. The treatment time selected was based on preliminary experiments in which the adsorption of EE2 was evaluated following one, two and three weeks of carbon treatment. In these experiments true equilibrium may not have been reached because the liquid-phase EE2 concentrations continued to decrease as treatment time increased. However, given that the calculated capacities at all three treatment times showed that EE2 was strongly adsorbed, a treatment time of three weeks was selected for use in future studies.

The isotherms presented in Figure 5 indicate that EE2 was strongly adsorbed by all three carbons, with Superdarco 12X40 having the highest capacity. This is reflected in the Freundlich Ks, which are the solid-phase capacities at a liquid phase concentration of 1µg/L at equilibrium. Figure 5 also shows that Hydrodarco 4000 has a much lower slope than the other two carbons. This could imply that at very low liquid phase concentrations, its capacity may be similar to the other two carbons.

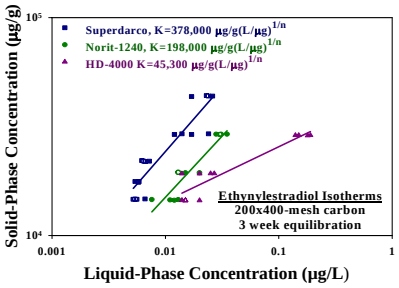

Figure 5. Bottle-Point Isotherms for Ethynylestradiol with Three Types of Carbon

The water sample concentrates from the isotherm studies were also evaluated using the MVLN assay. The correlation between the analytical results and the MVLN assay results for the isotherm samples is shown in Figure 6. The levels of estrogenic activity in the samples were converted to µg/L by comparison to a composite dose-response curve of EE2. The results of the MVLN assay were consistent with the analytical results for both the treated and untreated isotherm samples, as would be expected following adsorption onto GAC.

The correlation observed between the analytical results and the MVLN assay results for the isotherm samples indicates that the MVLN assay can be used to estimate the level of estrogenic compounds present in water samples before and after treatment. Consequently, if a significant discrepancy between the analytical results and the MVLN assay is observed, this would be an indication of changes in the target compound that occurred during the treatment process.

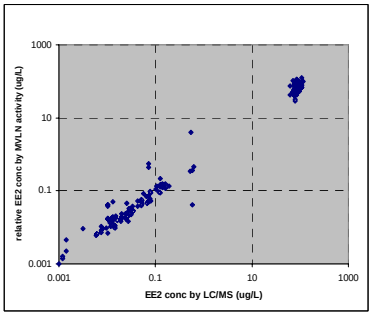

Figure 6. Comparison of Analytical and Estrogenic Activity Results

The isotherm studies, in addition to indicating that EE2 was strongly adsorbed to GAC, also suggest that the rate of adsorption was slow (equal to or greater than 3 weeks). To further investigate the GAC adsorption kinetics, column studies are being conducted. The data from the GAC column tests will be used to predict column breakthrough for full-scale drinking water treatment systems.

The results presented here indicate that EE2 is strongly adsorbed to GAC. However, the adsorption rates appear to be very slow. This may indicate that in drinking water treatment operations utilizing GAC with relatively short contact times, the slow adsorption kinetics of EE2 may lead to poor removal. The GAC adsorption kinetics data being generated in this study will provide information to allow for the optimization of GAC treatment for the removal of EE2, and other related EDCs, from surface waters.

Future Directions

The evaluation of GAC treatment for the removal of the steroid hormones by bench-scale isotherm and column studies will be continuing. Work has begun on the evaluation of the removal of steroid hormones through the coagulation process, one of the unit processes in conventional treatment. Conventional treatment is used by the majority of surface water treatment plants in the U.S. Consequently, information on the effectiveness of coagulation for the removal of EDCs from surface waters will be of use to the drinking water industry.

The ability of various drinking water treatment processes to remove a group of alkylphenolic compounds will be evaluated in the future. These compounds result from the biodegradation of alkylphenol polyethoxylates during sewage treatment and have been shown to be present in surface waters. An evaluation of their removal appears warranted given that they have been shown to be estrogenic in both *in vitro* and *in vivo* studies.